

# Investigation of Interaction in $C_{60}$ Embedded Complexes ( $X@C_{60}$ ) ( $X$ = Alkali or Halogen) at a Series of Radial Positions by Buckingham Potential Function

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## ABSTRACT

Two typical series of  $C_{60}$  embedded complexes ( $X@C_{60}$ ) ( $X$  = Li, Na, K, Rb, Cs; F, Cl, Br, I) have been chosen to study as prototypes, in which the Buckingham potential (exp-6-1) function was applied to calculating the interactions of the atom pairs. The potential parameters are obtained from related crystals by the simulations using molecular mechanics methods. To utilize the symmetry of the potential field in  $C_{60}$ , the calculation is carried out along five typical radial directions. The computational results show that the interaction between the embedded atom and the  $C_{60}$  cage is not purely electrostatic. The repulsive energy,  $E_{rep}$ , accounts for from 0.2% to 6.6% (for the alkali series), and from 1.5% to 58% (for the halogen series); the dispersive energy  $E_{dis}$  accounts for from 1.2% to 6.5% (for the alkali series), and from 2.2% to 42% (for the halogen series); and the electrostatic energy,  $E_{es}$ , accounts for 99% to 87% (for the alkali series) and from 96% to 0% (for the halogen series) when the embedded atom is put at the center of the cage.  $E_{rep}$  reaches up to 8% ~ 35% (alkali), and 16% ~ 74% (halogen);  $E_{dis}$  up to 4% ~ 16% (alkali) and 7% ~ 26% (halogen); and  $E_{es}$  falls down to about 88% ~ 49% (alkali), and 96% ~ 0% (halogen), when the embedded atom deviates 1.8 Å from the cage center. The total interactions,  $E_{inter}$ , are all attractive for  $X$  ( $X$  = Li, Na, K, Rb, Cs; F, Cl, Br), but repulsive for the I atom. It is shown that the potential field in the  $C_{60}$  cage has nearly spherical symmetry in an area with a radius of 1.8 Å around the cage center. The same kinds of interactions for the atoms in the two individual series are compared, and some variation rules are obtained. For ( $Li@C_{60}$ ), the minimum energy equilibrium point deviates from the center by about 0.5 Å. © 1996 by John Wiley & Sons, Inc.

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## Introduction

At present, although only a few C<sub>60</sub> and other fullerene embedded complexes have been obtained experimentally, it seems likely that many atoms, molecules, and even active radicals might be embedded into the C<sub>60</sub> cage and other fullerene cages, forming supermolecular embedded complexes with special properties and uses.<sup>1-9</sup> This has been a continuously active research area for some experimental and theoretical chemists. In this area, some new discoveries have successively been achieved in experiments,<sup>8-12</sup> while many theoretical investigations have also been carried out. The electronic and geometric structures for some kinds of embedded complexes have been given using theoretical methods,<sup>8,13-18</sup> and their stabilities have been predicted.<sup>17-23</sup>

One of the current viewpoints is that the interaction between the embedded atom and the C<sub>60</sub> cage is purely electrostatic.<sup>14,24-26</sup> In this work, we choose C<sub>60</sub> embedded complexes (X@C<sub>60</sub>) (X = alkali or halogen) as prototypes to be studied in which the embedded atoms (X) are two typical representatives in the periodic table. In the calculations, the Buckingham potential (exp-6-1) function is used,<sup>27</sup> and to utilize the symmetry of the potential field in the C<sub>60</sub> cage, the calculations are carried out along five typical radial directions.

## Geometric and Potential Parameters

### GEOMETRIC PARAMETERS

After the alkali or halogen atom is embedded in the C<sub>60</sub> cage, the original cage radius, long bond length, and short bond length of C<sub>60</sub> will change. To calculate the interaction between the embedded atom and the C<sub>60</sub> cage, it is necessary to know that the geometric parameters of C<sub>60</sub> with different embedded atoms.

We have optimized the geometric structure of C<sub>60</sub> with the quantum-chemical EHMO/ASED method,<sup>28-30</sup> which is an improved extended Hückel molecular orbital method with atomic superposition and electronic delocalization. In this method, the system energy is the sum of the energy of occupied molecular orbitals and the repulsive energy of atom pairs:

$$E = \sum_k O_k E_k + \sum_{ab} E_{r,ab} \quad (1)$$

where  $E_k$  and  $O_k$  are the energy and the occupation of the  $k$ th molecular orbital, and  $E_{r,ab}$  is the repulsive energy of atom pair  $a - b$ .  $E_k$  is obtained by solving the generalized Schrödinger eigenvalue equation:

$$HC = SCE \quad (2)$$

in which the diagonal and off-diagonal matrix elements of the Hamiltonian are:

$$H_{ii} = -(VSIP)_i \quad (3)$$

$$H_{ij} = 1.25(H_{ii} + H_{jj})S_{ij}\exp(-0.13R) \quad (4)$$

where  $VSIP$  is the valence-state ionization potential,  $R$  is the interatomic distance, and  $S_{ij}$  is the overlap integral. The repulsive energy,  $E_{r,ab}(R_b)$ , of  $b$  to  $a$  for any atom pair  $b - a$  in a molecule is taken into account:

$$E_{r,ab}(R_b) = Z_b \left( Z_a/R_b - \int dr \cdot \rho_a(r)/|r - R_b| \right) \quad (5)$$

where  $Z$ ,  $r$ , and  $R$  are atomic number, electron coordinate, and nuclear coordinate, respectively.

The EHMO/ASED method can predict molecular geometry and some other properties.<sup>28-30</sup> When this method is used for the endohedral complex system of (X@C<sub>60</sub>), the results obtained are in good agreement with the experimental and *ab initio* calculated results.<sup>16,17</sup> Furthermore, we have also optimized the geometric structure of the C<sub>60</sub> embedded complexes (X@C<sub>60</sub>) (X = alkali or halogen) with the embedded atom at the cage center or deviating from the center by different distances. When the deviation of the embedded atom from center is not too large, the changes of the optimized long bond length, short bond length, and cage radius can all be ignored.<sup>16-18</sup> These results are presented in Table I.

### POTENTIAL PARAMETERS

In the present article, the Buckingham potential (exp-6-1) function<sup>27</sup> is used to calculate the interaction of the embedded atom with the C<sub>60</sub> cage. The total interaction,  $E_{inter}$ , can be reduced to the sum of three terms<sup>31</sup>:

$$E_{inter} = E_{rep} + E_{dis} + E_{es} \quad (6)$$

where the subscripts *rep*, *dis*, and *es* stand for the repulsion owing to the electron cloud overlap,

**TABLE I.**  
**Geometry and Charge distribution of (X@C<sub>60</sub>)(Units: Å, |e|).**

(X@C <sub>60</sub> )	Short bond	Long bond	Cage Radius (R)	Charge (Q <sub>X</sub> )
Li	1.3901	1.4527	3.5440	+1
Na	1.3897	1.4498	3.5390	+1
K	1.3851	1.4463	3.5294	+1
Rb	1.3822	1.4432	3.5218	+1
Cs	1.3816	1.4428	3.5207	+1
F	1.3896	1.4557	3.5483	-1
Cl	1.3895	1.4563	3.5491	-1
Br	1.3900	1.4662	3.5494	-1
I	1.3941	1.4550	3.5512	0
None	1.3887	1.4568	3.5492	

dispersion, and electrostatic interaction, respectively. For these terms there are:

$$E_{rep} = \sum_i B_{X-C} \exp(-C_{X-C} R_i) \quad (7)$$

$$E_{dis} = \sum_i -A_{X-C} R_i^{-6} \quad (8)$$

$$E_{es} = \sum_i Q_X Q_C R_i^{-1} \quad (9)$$

where  $i$  is the index number of atom  $C$ ,  $Q_X$  and  $Q_C$  are the atomic charges on  $X$  and  $C$ , respectively, and  $R_i$  is the distance between the atom  $X$  and the  $i$ th atom,  $C$ .  $B_{X-C}$ ,  $C_{X-C}$ , and  $A_{X-C}$  are the corresponding potential parameters between the atom  $X$  and the  $i$ th atom  $C$ , respectively.

The relevant potential parameters of  $B_{X-C}$ ,  $C_{X-C}$ , and  $A_{X-C}$  ( $X = \text{Li, Na, K, Rb, Cs; F, Cl, Br, I}$ ) are obtained from the formulas:

$$B_{X-C} = (B_{X-X} \cdot B_{C-C})^{1/2} \quad (10)$$

$$C_{X-C} = \frac{1}{2}(C_{X-X} + C_{C-C}) \quad (11)$$

$$A_{X-C} = (A_{X-X} \cdot A_{C-C})^{1/2} \quad (12)$$

In the above three formulas,  $B_{C-C}$ ,  $C_{C-C}$ , and  $A_{C-C}$  are already known,<sup>25</sup> and  $B_{X-X}$ ,  $C_{X-X}$ , and  $A_{X-X}$  are obtained by means of a simulation using a molecular mechanics method<sup>32</sup> from the geometric and energetic parameters of the related crystals (LiCl, NaCl, KCl, RbCl, CsCl; NaF, NaCl, NaBr, NaI).<sup>33, 34</sup> To check the transferability and accuracy of the parameters obtained, the lattice energies of the related crystals were reproduced from the geometric and potential parameters obtained with the inverse of the above-mentioned process. The rele-

vant potential parameters obtained are shown in Table II.

### Interactions in (Alkali@C<sub>60</sub>)

The interactions between the embedded atoms  $X$  ( $X = \text{Li, Na, K, Rb, Cs}$ ) and the C<sub>60</sub> cage are first calculated using a Buckingham potential (exp-6-1) function. Because the C<sub>60</sub> cage is of  $I_h$  symmetry, but not spherical symmetry, five typical radial directions are chosen to calculate the interactions of the atom pair  $X-C$  to observe the symmetry of the potential field in the C<sub>60</sub> cage. The five typical radial directions are as follows:

- I—From the symmetrical center to the five-membered ring center on the cage surface.
- II—From the symmetrical center to the six-membered ring center on the cage surface.
- III—From the symmetrical center to the carbon atom on the cage surface.
- IV—From the symmetrical center to the long bond midpoint.
- V—From the symmetrical center to the short bond midpoint.

The calculations were carried out in the region of radial deviation  $r$  from 0 to 1.8 Å. The radius of the C<sub>60</sub> cage is about 3.5 Å, so, in this region, it is guaranteed that the distance between atom  $X$  and atom  $C$  is larger than the sum of their van der Waals radii.

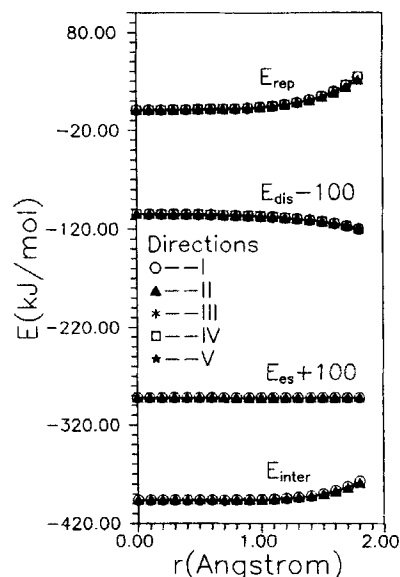
The calculated results show that the interactions along the five radial directions are not very different, therefore, it follows that the potential field of interaction can be considered as spherically symmetric in the region with a radius of 1.8 Å. As an

**TABLE II.**  
**Buckingham Potential Parameters Between C and X (X = Li, Na, K, Rb, Cs; F, Cl, Br, I).**

Atom Pair	Li—C	Na—C	K—C	Rb—C	Cs—C
A (kJ · Å <sup>6</sup> / mol)	156.828	373.780	689.781	867.123	934.565
B (kJ / mol)	14,122.952	13,008.542	11,791.062	11,058.562	10,215.256
C (Å <sup>-1</sup> )	3.950	3.493	3.045	2.868	2.818
Atom Pair	F—C	Cl—C	Br—C	I—C	
A (kJ · Å <sup>6</sup> / mol)	297.195	434.353	623.370	793.690	
B (kJ / mol)	5057.454	6923.655	8079.508	9257.125	
C (Å <sup>-1</sup> )	3.043	2.884	2.813	2.741	

example, the results of the embedded atom Li are shown in Figure 1. The situations of the other embedded atoms of X (X = Na, K, Rb, Cs) are similar to that of Li. In Table III are listed the maximum deviations,  $D_{\max}$ , and the average deviations,  $D_{\text{ave}}$ , along the five radial directions together with their relative values,  $D_{\max}/|E|$  and  $D_{\text{ave}}/|E|$ , where  $|E|$  is the absolute value of the interaction energy.

If we define the interaction energy,  $E_t$ , as the sum of ( $|E_{\text{rep}}| + |E_{\text{dis}}| + |E_{\text{es}}|$ ), then from Figure 1 it is seen that when the embedded atom Li is at the cage center, the repulsive energy,  $E_{\text{rep}}$ , and the dispersive energy,  $E_{\text{dis}}$ , in  $E_t$  are  $|E_{\text{rep}}|/E_t \sim 0.2\%$  and  $|E_{\text{dis}}|/E_t \sim 1.2\%$ , respectively, and the electrostatic energy  $E_{\text{es}}$  in  $E_t$  is  $|E_{\text{es}}|/E_t \sim 98\%$ . When the embedded Li atom is at a position deviating 1.8 Å from the cage center,  $E_{\text{rep}}$  in  $E_t$  and  $E_{\text{dis}}$  in  $E_t$  are  $|E_{\text{rep}}|/E_t \sim 8\%$  and  $|E_{\text{dis}}|/E_t \sim 4\%$ , respectively, and  $E_{\text{es}}$  in  $E_t$  is  $|E_{\text{es}}|/E_t \sim 88\%$ . The situa-

**FIGURE 1.** Curves of various interactions vs.  $r$  for (Li@C<sub>60</sub>).**TABLE III.**  
**Average Deviation ( $D_{\text{ave}}$ ) and Maximum Deviation ( $D_{\max}$ ) (kJ / mol).**

		Li		Na		K		Rb		Cs	
		$D_{\text{ave}}$	$D_{\max}$	$D_{\text{ave}}$	$D_{\max}$	$D_{\text{ave}}$	$D_{\max}$	$D_{\text{ave}}$	$D_{\max}$	$D_{\text{ave}}$	$D_{\max}$
$E_{\text{rep}}$	A <sup>a</sup>	0.53	3.01	1.00	5.86	1.88	10.6	2.35	13.1	2.34	13.0
	R <sup>b</sup>	0.07	0.09	0.05	0.07	0.03	0.05	0.03	0.05	0.03	0.05
$E_{\text{dis}}$	A	0.18	0.94	0.41	2.31	0.76	4.41	1.02	5.7	1.03	6.2
	R	0.02	0.05	0.03	0.05	0.02	0.05	0.02	0.05	0.02	0.05
$E_{\text{es}}$	A	0.06	0.26	0.07	0.27	0.07	0.27	0.07	0.3	0.07	0.3
	R	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$E_{\text{inter}}$	A	0.35	1.81	0.60	3.28	1.09	6.0	1.44	7.1	1.34	6.5
	R	0.00	0.01	0.02	0.01	0.00	0.02	0.00	0.03	0.00	0.02

<sup>a</sup> A ~ absolute value.<sup>b</sup> R ~ relative value.

tions of the other embedded atoms  $X$  ( $X = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ ) are similar to that for  $\text{Li}$ . From these data, it can be concluded that generally speaking, the potential field is not purely electrostatic around the  $\text{C}_{60}$  cage center.

In Figure 2a-d are given the  $E_{\text{rep}} \sim r$ ,  $E_{\text{dis}} \sim r$ ,  $E_{\text{es}} \sim r$ , and  $E_{\text{inter}} \sim r$  curves for all alkali atoms,  $X$  ( $X = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ ), in which the data run along the radial axis from the cage center to the center of the five-membered ring. From these figures it is seen that the variation of  $E_{\text{rep}}$  with  $r$  is the fastest, and the variation of  $E_{\text{es}}$  is the slowest. These results can easily be explained by the forms of the functions,  $E_{\text{rep}}$  being an exponential function of  $(-r)$ ,  $E_{\text{dis}}$  a  $(-6)$  power function of  $r$  and  $E_{\text{es}}$  a  $(-1)$  power function of  $r$ .

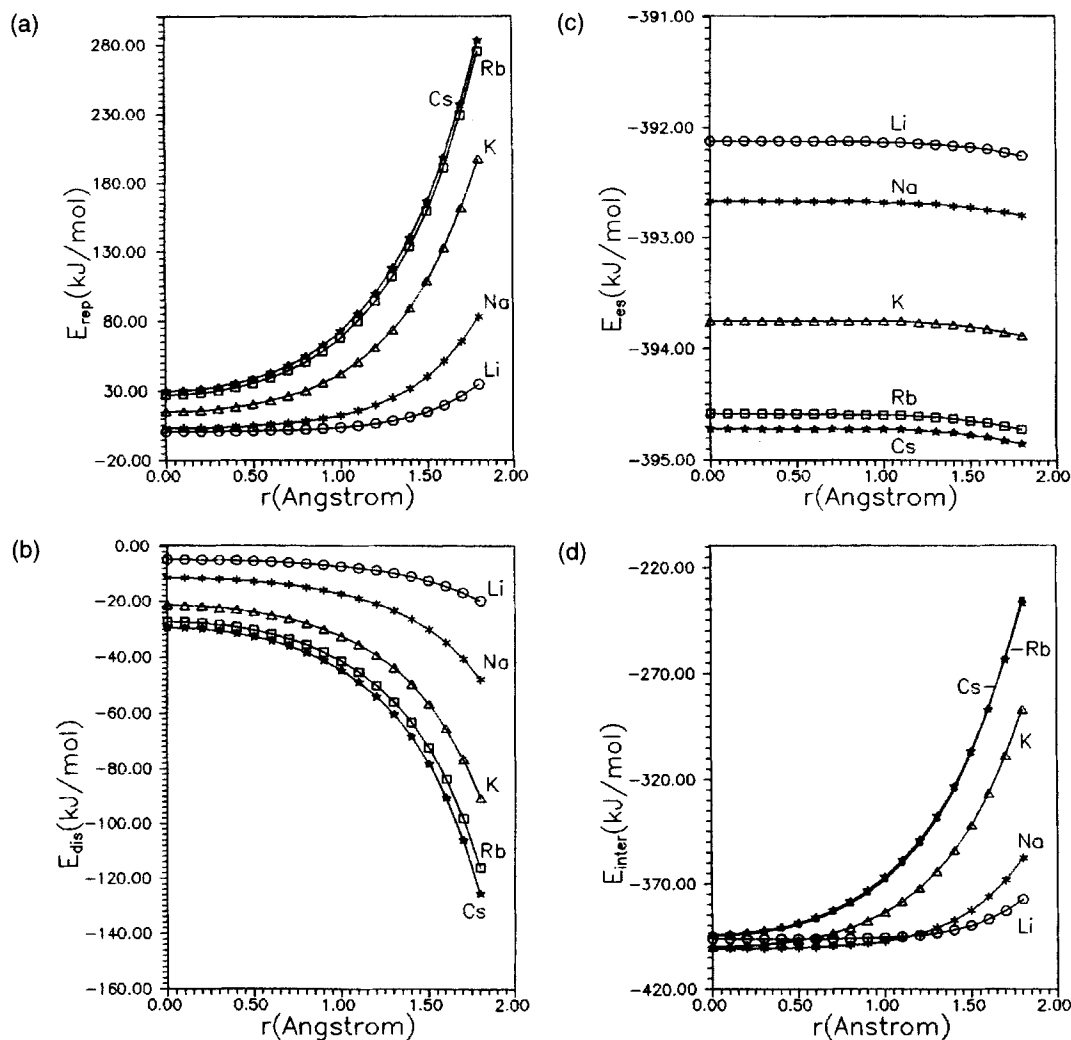
It is easily seen from Figure 2a-d that the rules in  $E_{\text{rep}}$  are:

$$|E_{\text{rep}}|_{\text{Cs}} > |E_{\text{rep}}|_{\text{Rb}} > |E_{\text{rep}}|_{\text{K}} > |E_{\text{rep}}|_{\text{Na}} > |E_{\text{rep}}|_{\text{Li}} \quad (13)$$

and

$$\left( \frac{d|E_{\text{rep}}|}{dr} \right)_{\text{Cs}} > \left( \frac{d|E_{\text{rep}}|}{dr} \right)_{\text{Rb}} > \left( \frac{d|E_{\text{rep}}|}{dr} \right)_{\text{K}} > \left( \frac{d|E_{\text{rep}}|}{dr} \right)_{\text{Na}} > \left( \frac{d|E_{\text{rep}}|}{dr} \right)_{\text{Li}} \quad (14)$$

where the reason for this can be found from the potential parameters  $B_{X-C}$  and  $C_{X-C}$  of the atom pairs  $X-C$  ( $X = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ ) (Table II).



**FIGURE 2.** (a) Curves of  $E_{\text{rep}} \sim r$  for  $(\text{Alkali}@\text{C}_{60})$ . (b) Curves of  $E_{\text{dis}} \sim r$  for  $(\text{Alkali}@\text{C}_{60})$ . (c) Curves of  $E_{\text{es}} \sim r$  for  $(\text{Alkali}@\text{C}_{60})$ . (d) Curves of  $E_{\text{inter}} \sim r$  for  $(\text{Alkali}@\text{C}_{60})$ .

For the  $E_{dis}$ , there are similar rules as those in  $E_{rep}$ :

$$|E_{dis}|_{Cs} > |E_{dis}|_{Rb} > |E_{dis}|_K > |E_{dis}|_{Na} > |E_{dis}|_{Li} \quad (15)$$

and

$$\left(\frac{d|E_{dis}|}{dr}\right)_{Cs} > \left(\frac{d|E_{dis}|}{dr}\right)_{Rb} > \left(\frac{d|E_{dis}|}{dr}\right)_K > \left(\frac{d|E_{dis}|}{dr}\right)_{Na} > \left(\frac{d|E_{dis}|}{dr}\right)_{Li} \quad (16)$$

and the reason for this can also be found from the potential parameters  $A_{X-C}$  of the atom pairs  $X-C$  ( $X = Li, Na, K, Rb, Cs$ ) (Table II).

For  $E_{es}$ , its variation rules are different from the above:

$$|E_{es}|_{Cs} \geq |E_{es}|_{Rb} \geq |E_{es}|_K \geq |E_{es}|_{Na} \geq |E_{es}|_{Li} \quad (17)$$

and

$$\left(\frac{d|E_{es}|}{dr}\right)_{Cs} \approx \left(\frac{d|E_{es}|}{dr}\right)_{Rb} \approx \left(\frac{d|E_{es}|}{dr}\right)_K \approx \left(\frac{d|E_{es}|}{dr}\right)_{Na} \approx \left(\frac{d|E_{es}|}{dr}\right)_{Li} \quad (18)$$

The variations of  $E_{es}$  with changes in  $r$  are nearly equal to zero for all of the alkaline elements. The reason can be understood from the small difference in the cage radii of ( $X@C_{60}$ ), and the same charges on  $X$  ( $X = Li, Na, K, Rb, Cs$ ) (Table I).

As for the total interaction,  $E_{inter}$ , there are variation rules as follows:

$$|E_{inter}|_{Cs} \approx |E_{inter}|_{Rb} < |E_{inter}|_K < |E_{inter}|_{Na} < |E_{inter}|_{Li} \quad (19)$$

(Correct for Li only when  $r \geq \sim 1.2\text{\AA}$ ) and

$$\begin{aligned} \left(\frac{d|E_{inter}|}{dr}\right)_{Cs} &\approx \left(\frac{d|E_{inter}|}{dr}\right)_{Rb} \\ &> \left(\frac{d|E_{inter}|}{dr}\right)_K > \left(\frac{d|E_{inter}|}{dr}\right)_{Na} \\ &> \left(\frac{d|E_{inter}|}{dr}\right)_{Li} \end{aligned} \quad (20)$$

In the alkali series, ( $Li@C_{60}$ ) is different from the others, namely, the total interaction between the Li and  $C_{60}$  cage in the range ( $r < 1.2\text{\AA}$ ) is not the lowest among those of the five atoms. Its total interaction does not change monotonically with the  $r$ , and its curve crosses those of Na and K. On its curve, there exists a minimum point deviating from the cage center by about  $0.5\text{\AA}$ , which can be seen clearly in Table IV. This phenomenon can be easily understood from the variation trends of the three components in  $E_{inter}$ ; i.e., the trends of  $E_{rep} \sim r$ ,  $E_{dis} \sim r$ , and  $E_{es} \sim r$ . Therefore, one finds that the minimum point of Li results from the net effect of the different variation trends of the three terms. The reason only Li has a minimum point on its potential energy curve is that it has the smallest atomic radius, and the largest repulsive potential parameters (B and C) and the smallest dispersive potential parameter (A). Owing to the combination of those two sets of potential parameters, for the  $E_{inter}$  curve, the variation trend in the region with smaller  $r$  is determined by the dispersive energy, but the variation trend in the region with larger  $r$  is determined by the repulsive energy. For the other embedded atoms  $X$  ( $X = Na, K, Rb, Cs$ ), the variations of  $E_{inter}$  with  $r$  are all monotonic.

### Interactions in (Halogen@C<sub>60</sub>)

Similarly, the calculated results of this complex series also show that the interactions along the five

**TABLE IV.**  $E_{inter}$  in ( $Li@C_{60}$ ) Along Direction From Cage Center to Five-membered Ring Center (Units:  $\text{\AA}$ , kJ/mol).

$r$	0.0	0.1	0.2	0.3	0.4	0.5	0.6
$E_{inter}$	-396.165	-396.168	-396.177	-396.189	-396.200	-396.203	-396.190
$r$	0.7	0.8	0.9	1.0	1.1	1.2	1.3
$E_{inter}$	-396.146	-396.053	-395.882	-395.597	-395.147	-394.460	-393.443
$r$	1.4	1.5	1.6	1.7	1.8		
$E_{inter}$	-391.968	-389.872	-386.940	-382.905	-377.438		

radial directions are all nearly equal, indicating that the potential field of interaction in  $C_{60}$  can be considered as spherically symmetric in the region of radius 1.8 Å. Here we choose ( $F@C_{60}$ ) as an example to illustrate the variation curves of the different interactions in Figure 3. For the other embedded atoms, such as Cl, Br, and I, there are similar results to those of F. Similar to Table IV, in Table V are listed the corresponding maximum deviations,  $D_{max}$ , and the average deviations,  $D_{ave}$ , along the five radial directions, together with their relative values  $D_{max}/|E|$  and  $D_{ave}/|E|$ .

From Figure 3, it can be seen that when the embedded atom F is at the cage center, the repulsive energy,  $E_{rep}$ , and the dispersive energy,  $E_{dis}$ , in  $E_t (= |E_{rep}| + |E_{dis}| + |E_{es}|)$  amount to  $|E_{rep}|/E_t \sim 1.5\%$  and  $|E_{dis}|/E_t \sim 2.2\%$ , respectively, and the electrostatic energy,  $E_{es}$ , in  $E_t$  is  $|E_{es}|/E_t \sim 96\%$ . When the embedded F atom is at the position of 1.8 Å deviating from the cage center,  $E_{rep}$  in  $E_t$  and  $E_{dis}$  in  $E_t$  are  $|E_{rep}|/E_t \sim 16\%$  and  $|E_{dis}|/E_t \sim 7\%$ , respectively, and  $E_{es}$  in  $E_t$  is  $\sim E_{es}/E_t \sim 77\%$ . The situations of the other embedded halogen atoms are similar to that of F. From these data it also can be concluded that, generally speaking, the potential field is not purely electrostatic in the  $C_{60}$  cage.

There is a peculiarity that exists in ( $I@C_{60}$ )—that is, I and  $C_{60}$  are both neutral without charge transfer between them when they form a complex such as ( $I@C_{60}$ ), and the interaction between I and  $C_{60}$  has no electrostatic term in it. Also we have the result of  $|E_{rep}| > |E_{dis}|$ . Therefore, the values of  $E_{inter}$  are always positive, namely, the total interaction is repulsive.

In Figure 4a–d are given the  $E_{rep} \sim r$ ,  $E_{dis} \sim r$ ,  $E_{es} \sim r$ , and  $E_{inter} \sim r$  curves for all of the halo-

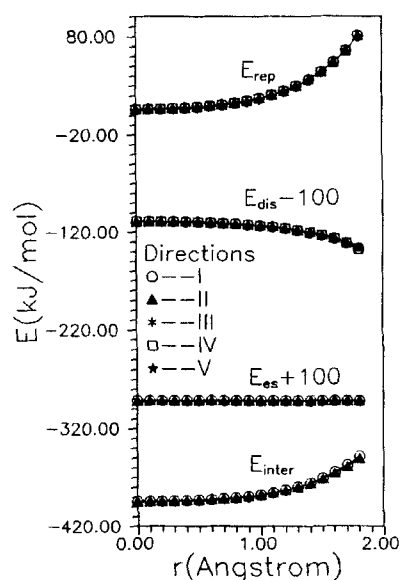


FIGURE 3. Curves of various interactions vs.  $r$  for ( $F@C_{60}$ ).

gen atoms  $X$  ( $X = F, Cl, Br, I$ ), in which the data are also chosen along the radial axis from the cage center to the center of the five-membered ring. From these figures it is seen that the variation of  $E_{rep}$  with  $r$  is the fastest, and the variation of  $E_{es}$  is the slowest. These are determined by their forms of the functions, in which  $E_{rep}$  is an exponential function of  $(-r)$ ,  $E_{dis}$  a  $(-6)$  power function of  $r$ , and  $E_{es}$  a  $(-1)$  power function of  $r$ .

For the  $E_{rep}$ , from Figure 4a–d it can be seen easily that:

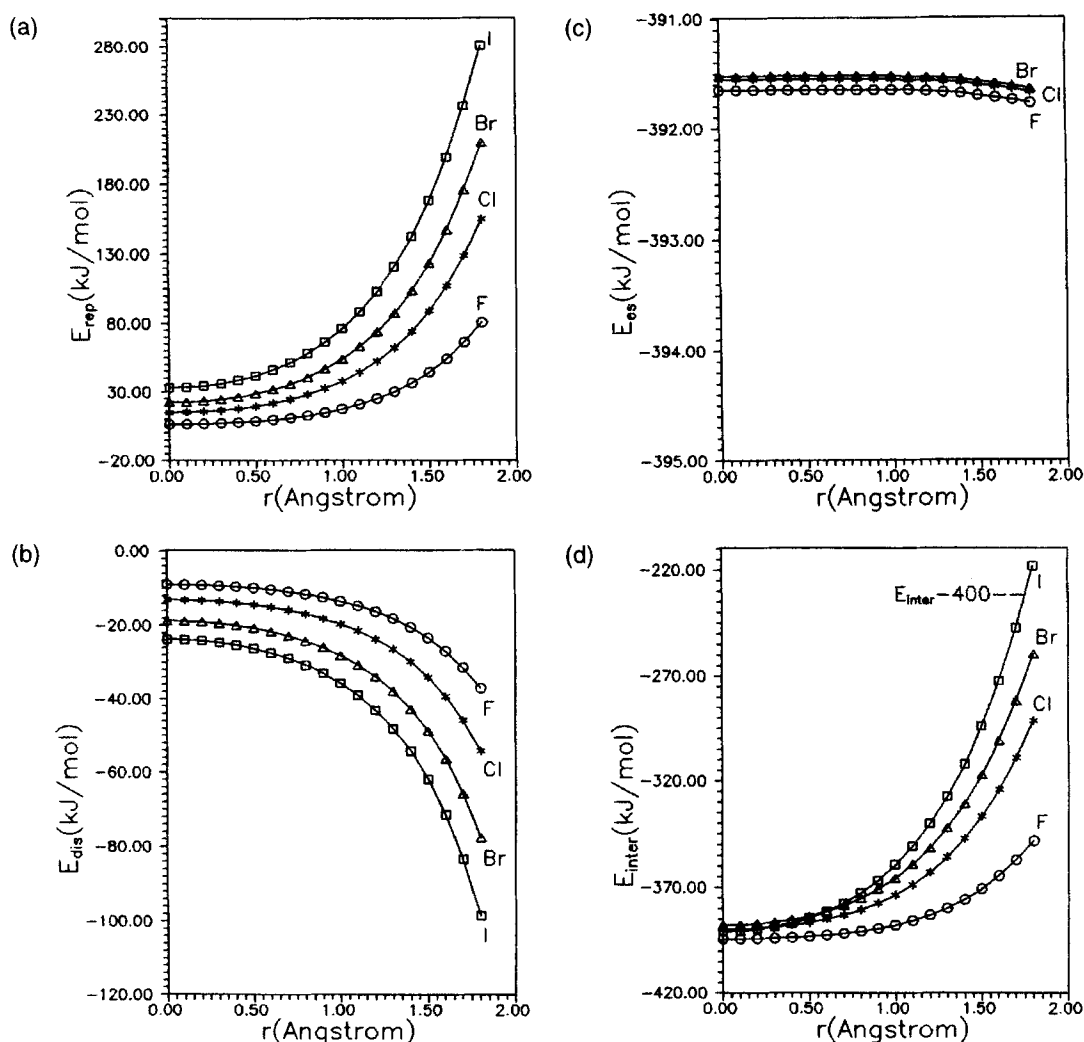
$$\begin{aligned} |E_{rep}|_I &> |E_{rep}|_{Br} \\ &> |E_{rep}|_{Cl} > |E_{rep}|_F \end{aligned} \quad (21)$$

TABLE V.  
Average Deviation ( $D_{ave}$ ) and Maximum Deviation ( $D_{max}$ ) (kJ/mol).

		F		Cl		Br		I	
		$D_{ave}$	$D_{max}$	$D_{ave}$	$D_{max}$	$D_{ave}$	$D_{max}$	$D_{ave}$	$D_{max}$
$E_{rep}$	A <sup>a</sup>	0.74	4.21	1.29	7.18	1.67	9.27	2.17	11.99
	R <sup>b</sup>	0.03	0.05	0.03	0.05	0.02	0.04	0.00	0.04
$E_{dis}$	A	0.31	1.72	0.45	2.50	0.64	3.59	0.78	4.67
	R	0.02	0.05	0.02	0.05	0.02	0.05	0.02	0.05
$E_{es}$	A	0.06	0.26	0.06	0.25	0.07	0.26	0.00	0.00
	R	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$E_{inter}$	A	0.43	2.23	0.93	4.42	1.09	5.42	1.39	7.33
	R	0.00	0.01	0.00	0.02	0.00	0.02	0.02	0.04

<sup>a</sup>A ~ absolute values.

<sup>b</sup>R ~ relative values.



**FIGURE 4.** (a) Curves of  $E_{\text{rep}} \sim r$  for (Halogen@C<sub>60</sub>). (b) Curves of  $E_{\text{dis}} \sim r$  for (Halogen@C<sub>60</sub>). (c) Curves of  $E_{\text{es}} \sim r$  for (Halogen@C<sub>60</sub>). (d) Curves of  $E_{\text{inter}} \sim r$  for (Halogen@C<sub>60</sub>).

and

$$\left( \frac{d|E_{\text{rep}}|}{dr} \right)_I > \left( \frac{d|E_{\text{rep}}|}{dr} \right)_{\text{Br}} > \left( \frac{d|E_{\text{rep}}|}{dr} \right)_{\text{Cl}} > \left( \frac{d|E_{\text{rep}}|}{dr} \right)_F \quad (22)$$

These results can be understood from the potential parameters  $B_{X-C}$  and  $C_{X-C}$  of the atom pairs X—C (X = F, Cl, Br, I) (Table II).

For  $E_{\text{dis}}$  in this halogen complex series, there are similar variation rules to eqs. (13) and (14) as follows:

$$|E_{\text{dis}}|_I > |E_{\text{dis}}|_{\text{Br}} > |E_{\text{dis}}|_{\text{Cl}} > |E_{\text{dis}}|_F \quad (23)$$

and

$$\left( \frac{d|E_{\text{dis}}|}{dr} \right)_I > \left( \frac{d|E_{\text{dis}}|}{dr} \right)_{\text{Br}} > \left( \frac{d|E_{\text{dis}}|}{dr} \right)_{\text{Cl}} > \left( \frac{d|E_{\text{dis}}|}{dr} \right)_F \quad (24)$$

where the reason for this can also be found from the potential parameters  $A_{X-C}$  of the atom pairs X—C (X = F, Cl, Br, I) (Table II).

For the  $E_{\text{es}}$ , the rules are different from those given above:

$$0 = |E_{\text{es}}|_I < |E_{\text{es}}|_{\text{Br}} \leq |E_{\text{es}}|_{\text{Cl}} \leq |E_{\text{es}}|_F \quad (25)$$



and

$$\left(\frac{d|E_{es}|}{dr}\right)_{Br} \approx \left(\frac{d|E_{es}|}{dr}\right)_{Cl} \approx \left(\frac{d|E_{es}|}{dr}\right)_F \quad (26)$$

The variations of  $E_{es}$  with  $r$  are all nearly equal to zero in this complex series, and the reason can be seen from the similar cage radii of ( $X@C_{60}$ ) and the same charge on  $X$  ( $X = F, Cl, Br$ ) (Table I).

For the total interaction, the variation presents an order similar to that of the alkali series. However, there is a special case that the total interaction energy of ( $I@C_{60}$ ) is always positive with a much higher value. The total interaction  $E_{inter}$  values in the system of (halogen@ $C_{60}$ ) observe the rules as follows:

$$|E_{inter}|_I < |E_{inter}|_{Br} < |E_{inter}|_{Cl} < |E_{inter}|_F \quad (27)$$

and

$$\begin{aligned} \left(\frac{d|E_{inter}|}{dr}\right)_I &> \left(\frac{d|E_{inter}|}{dr}\right)_{Br} \\ &> \left(\frac{d|E_{inter}|}{dr}\right)_{Cl} > \left(\frac{d|E_{inter}|}{dr}\right)_F \end{aligned} \quad (28)$$

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